(19) BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENT- UND MARKENAMT

(12) **Offenlegungsschrift**

(10) **DE 198 45 519 A 1**

(51) Int. Cl.[7]:
B 32 B 27/08
B 32 B 27/28
A 22 C 13/00

(21) Aktenzeichen: 198 45 519.4
(22) Anmeldetag: 2. 10. 1998
(43) Offenlegungstag: 6. 4. 2000

= EP 993 940

DE 198 45 519 A 1

(71) Anmelder:
Kalle Nalo GmbH & Co. KG, 65203 Wiesbaden, DE

(74) Vertreter:
Zounek, N., Dipl.-Ing., Pat.-Anw., 65203 Wiesbaden

(72) Erfinder:
Grolig, Gerhard, Dr., 64546 Mörfelden-Walldorf, DE; Hiltmann, Klaus, 65203 Wiesbaden, DE; Kummer, Thomas, 65232 Taunusstein, DE

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Schrumpffähige, kaschierte Folie mit verbesserter Barrierewirkung und daraus hergestellte Schlauchfolie mit Siegelnaht

(57) Die Erfindung betrifft eine heißschrumpffähige, kaschierte oder beschichtete Kunststoffolie, die ein- oder beidseitig eine heißsiegelfähige Polyethylen-, Polypropylen- oder Ethylen/Propylen-Copolymerschicht sowie eine Schicht aus Polyethylenterephthalat, Polyamid oder Polypropylen besitzt, die mindestens eine Schicht aus einem anorganisch-organischen Hybridpolymer oder eine SiO_x-Schicht aufweist. Die Folie besitzt eine hohe Barrierewirkung für (Luft-)Sauerstoff und Wasserdampf. Sie ist allgemein transparent, kann jedoch auch eingefärbt und/oder bedruckt sein. Durch Heißsiegeln werden aus der Flachfolie Schlauchfolien mit Siegelnaht hergestellt. Diese eignen sich als Nahrungsmittelhüllen, insbesondere für Brüh- und Kochwürste, daneben auch aus Umhüllung für Tiernahrung.

DE 198 45 519 A 1

TRANSLATION OF EP-A 993 940

= DE 198 45 519

Shrinkable, laminated or coated film with improved barrier effectiveness, and a film tube produced therefrom with a welded seam

The invention relates to a heat-shrinkable, laminated or coated plastic film which has, on one or both sides, a heat-sealable polyethylene, polypropylene or ethylene-propylene copolymer layer, and also has a layer of polyethylene terephthalate, polyamide or polypropylene. It further relates to a tube produced therefrom, which can in particular be used as a casing for foods.

Laminated plastic films having more than one layer are known. They include, for example, a film in which one layer of polyethylene (PE) and one of polyamide (PA) have been bonded to one another via a layer of a hot-melt adhesive based on polyurethane or on poly(ethyl acrylate/methacrylate). They also include a film which has a central polyamide layer and a polyethylene layer at each surface. Two layers of the hot-melt adhesive mentioned bond the individual layers to one another. Instead of the hot-melt adhesive there may also be layers of ethylene-vinyl acetate (EVA) copolymers. A five-layered casing of symmetrical structure is therefore possible, with a central layer of polyvinylidene chloride (PVDC), on each side of which there is firstly an EVA tie layer and then a PE layer.

Tubes can be produced from these known films by heat-sealing. However, these tubes have not gained acceptance as synthetic sausage-casings since their recovery after stuffing and after scalding, and, respectively, cooking of the sausage is inadequate, and they have insufficient barrier effectiveness for (atmospheric) oxygen and water vapor, and also poor adhesion of the inner layer to the sausage emulsion. After 15 min in water at 80°C longitudinal shrinkage is at best 4% and transverse shrinkage is at best 2%. As a result, the casing separates from the emulsion during the course of sausage manufacture, i.e. the casing "releases". The oxygen permeability (in accordance with DIN 53 380) of the casing tubes produced from known laminated films having more than one layer is generally from 27 to 31 cm^3/m^2 d bar or higher still. The water vapor permeability (in accordance with DIN 53 122) is from 2 to 3 g/m^2 d or poorer.

Sausage-casings which can be produced from a flat film continue to have particular attraction, since they can be produced immediately prior to stuffing (for example with the aid of a shaping tool and sealing apparatus), so that no shirring of the casing is required. Prefabricated sausage-casings, in contrast, usually have to be supplied as so-called shirred sticks, which then have to be pushed over the stuffing tube, and the casing is then "de-shirred" during stuffing. The shirring of sections of the casing gives rise to additional costs. In addition, depending on caliber, the shirred stick comprises no more than 30 to 70 m of sausage-casing. A flat film, however, can be supplied wound up in considerably greater lengths. This means that correspondingly longer sections can be manufactured and stuffed, giving cost advantages. In addition, a flat film is more cost effective to produce than a film tube.

The object was therefore to provide a flat film which does not have the disadvantages described above and which can be processed in a simple manner to give a tubular casing. The casing should have the properties required for sausage-casings, i.e. have flexibility and sufficient shrinkability so that the casing is at all times in tight contact with the sausage emulsion, and should at the same time have high barrier effectiveness for oxygen and water vapor. In addition, the casing should also reliably prevent escape of flavors from the sausage emulsion. A final further requirement is consistent calibration, to permit the production of sausages with uniform diameter.

The object has been achieved by means of a film having more than one layer in which silica-containing layers have been arranged between the separate layers. The layers with or of silica act as barrier layers for oxygen and water vapor, and specifically and surprisingly are substantially better for this than layers of the same thickness of organic polymers, such as polyethylene terephthalate (PET).

The present application therefore provides a heat-shrinkable, laminated or coated plastic film which has, on one or both sides, a heat-sealable polyethylene, polypropylene or ethylene-propylene copolymer layer, and also has a layer of polyethylene terephthalate, polyamide or polypropylene, wherein the film has at

least one layer of an inorganic-organic hybrid polymer or has an SiO_x layer. Both types of layer comprise silicon, where the silicon atoms have bonding to oxygen atoms, and act as barriers for (atmospheric) oxygen and water vapor. The inorganic-organic hybrid polymer here acts at the same time as a laminating adhesive. The thickness of the hybrid polymer layer is from 0.5 to 10 µm, preferably from 2 to 7 µm, particularly preferably about 5 µm. If an SiO_x layer is present instead of the layer of the inorganic-organic hybrid polymer, the adhesion is provided by a layer of a conventional laminating adhesive, preferably based on polyurethane or on ethyl acrylate/methacrylate copolymers. If a particularly high level of barrier effectiveness is desired it is, of course, also possible for a layer of the inorganic-organic hybrid polymer to follow directly onto the SiO_x layer. The SiO_x layer is preferably in direct contact with the PET, PA or PP layer, but it may also have been applied to the inward-facing or outward-facing layer on their sides facing toward the laminating-adhesive layer. It is generally produced by vapor-deposition or a similar process and is therefore significantly thinner than the layer of the inorganic-organic hybrid polymer. The thickness of the SiO_x layer is generally from 10 to 80 nm, preferably from 20 to 50 nm. It will be clear from the above that the novel film may also have more than one layer of the inorganic-organic hybrid polymer and/or more than one SiO_x layer. The total number of hybrid polymer and silica layers is, however, preferably not more than 3.

The thickness of the (co)polymer layer on the inward-facing and, respectively, outward-facing side of the film is, in contrast, from 5 to 30 µm, preferably from 6 to 15 µm. In the case of films sealable on only one side, the nonsealable side is preferably produced from a polyamide layer, in particular from a polyamide as has also been mentioned for the nonsealable layer. Particular preference is given to a laminated film with a symmetrical structure which in each case has an adhesive layer based on inorganic-organic hybrid polymers between the nonsealable layer and the inward facing and, respectively, outward-facing polyolefin layers. Preference is also given to films with heat-sealable polymer layers on both their inward-facing and outward-facing sides. This embodiment is also advantageous in heat-sealing (the inward-facing side can be sealed to the outward-facing side in the areas of overlap). Preference is also given to a symmetrically constructed

film in which the nonsealable layer has been provided on both sides with an SiO_x layer followed by a layer of a conventional laminating adhesive. The SiO_x layer is preferably applied by vapor-deposition or plasma-coating. SiO_x layers and ormocer adhesive layers may also be present simultaneously. This gives a particularly high level of barrier effectiveness.

Suitable inorganic-organic hybrid polymers are known and are termed ormocers (organically modified ceramics) and are described, for example, in EP-A 580 487. They generally have the empirical formula $C_nH_mO_xSi_yMe_z$, where Me is a metal of the 3rd or 4th main group, or of the 3rd, 4th, 5th or 6th transition group of the Periodic Table. Preference is given to aluminum, silicon, titanium, zirconium, hafnium, tantalum or tungsten. n is generally a number from 4 to 48, m is a number from 5 to 52, x is a number from 5 to 48 and y is a number from 2 to 16, while z is 1. The ratio n:(y+z), i.e. the ratio carbon:(silicon + metal), is generally less than 7, preferably less than 5. Ormocers are preferably prepared by the sol-gel process. This process begins by preparing a sol by controlled hydrolysis and condensation of organoalkoxysilanes, if desired with addition of metal alcoholates (such as titanium tetraalcoholate, specifically titanium tetrabutylate) and/or of tetraalkoxysilanes, and the sol is then converted into the inorganic-organic hybrid polymer by thermal or UV-induced polymerization. The inorganic-organic hybrid polymers are generally applied with the aid of an organic solvent. Particular solvents are: ethyl acetate, ethyl lactate and others acceptable under food legislation.

The sealable layers of polyethylene and/or polypropylene or of ethylene-propylene copolymers on the outward-facing and inward-facing surfaces are preferably composed of a polyethylene or polypropylene. Particular preference is given to low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) or high-density polyethylene (HDPE), or mixtures of these. Polyethylenes which have proven particularly useful are those which were prepared using metallocene catalysts. The inward-facing and the outward-facing layers are biaxially oriented prior to lamination, specifically with an area stretching

ratio of from 1:2 to 1:20, preferably from 1:5 to 1:10. The materials of the inward-facing and outward-facing layers may differ.

The nonsealable layers are preferably composed of nylon-6, polyhexamethyleneadipamide (= nylon-6,6), nylon-11, nylon-12 or polyethylene terephthalate. They are also biaxially oriented and should essentially have the same shrinkage properties as the outer layers, so that no delamination or distortion occurs on shrinking. The principal function of the nonsealable layer is to give the film the required mechanical strength. A layer of biaxially oriented polypropylene (BOPP) is therefore also suitable. In a preferred embodiment SiO_x has been vacuum-deposited onto one or both sides of the nonsealable layer. The SiO_x coating may also be produced by plasma polymerization. This coating can markedly improve the barrier properties of the multilayer film. The nonsealable layer may also comprise pigments, e.g. TiO_2 particles or other pigments, in amounts sufficient to give effective pigmentation. The nonsealable layer may itself have a structure of more than one layer.

The novel film may have other layers, but these generally do not confer any particular advantage, but merely increase costs. It is also possible for an SiO_x coating and an ormocer tie layer to be present simultaneously. This means, for example, that the nonsealable layer has SiO_x vapor-deposited on one side, while the other side has an adhesive layer of ormocer.

Laminating processes for producing the novel multilayer film are known per se to the person skilled in the art. Doubling processes are particularly preferred.

The novel film has shrinkage of from 5 to 15%, preferably about 10%, in both longitudinal and transverse directions (after storage for 15 min in water at 80°C). This ensures that the sausage has a plump appearance and an attractive shape. Oxygen permeability (DIN 53 380) is not more than 10 cm^3/m^2 d bar, and water-vapor permeability is not more than 1 g/m^2 d. To make the film printable its surface tension should not be less than 40 dyn. A surface tension of this type may be achieved by corona-treatment of the outward-facing layer (e.g. of a

polyethylene layer) prior to lamination. Prior to, or else after, lamination the separate layers may be printed in one or more colors. Processes particularly suitable for this are copper gravure printing, flexographic printing and revoprint.

To produce a film tube, the novel multilayer film is cut into strips, which are then shaped with the aid of a shaping tool to give a tube whose longitudinal edges overlap. The edges are then bonded firmly to one another by exposing the film to heat and pressure in a sealing apparatus. Further processing of the film tube (e.g. stuffing with sausage emulsion and portioning) can take place immediately following its production, and also in a single piece of equipment, for example in a transfer sealing machine. There is then no need to shirr the finished casing.

The excellent barrier properties of the novel film tube make it particularly suitable as a casing for foodstuffs, in particular as a synthetic sausage-casing. The sausage-casing may be used with particular advantage for types of sausage which discolor easily when exposed to air, for example liver sausage. The film tubes are also particularly suitable for producing scalded-emulsion sausages and animal feed (pet food). They are transparent or have pigmentation and/or printing, as required by the application. The printing ink is preferably introduced into the intermediate layer so that it does not come into contact with the filling and is not subject to external influences. Casings for animal feed, however, usually have pigmentation. The particularly good barrier properties of the casing mean that scalded-emulsion sausages can be stored for up to 3 months and animal feed for as long as 12 months.

<u>Example</u>

a) Using an application system, a heated solvent-containing laminating adhesive (ormocer) was applied in the form of a thin layer to a film made from a mixture of LDPE and LLDPE of thickness 20 μm, and was dried. A high-shrinkage nylon-6,6 film was then laminated to this adhesive layer. The weight per unit area of the adhesive layer after drying was about 2.5 g/m^2.

b) Another ormocer layer of practically identical weight per unit area was applied as described under a) to the PA layer of this composite. A film made from a mixture of LDPE and LLDPE was in turn laminated to this adhesive layer.

After 15 min storage in water at 80°C, the film having more than one layer and produced in this way had a shrinkage of about 10% in longitudinal and transverse directions. Its oxygen permeability in accordance with DIN 53380 was about 10 cm^3/m^2 d bar, and its water-vapor permeability in accordance with DIN 53122 was about 1.0 g per square meter and day.

This film was shaped in-line on a transfer sealing machine to give a tube, the overlapping edges were sealed, the resultant tube was stuffed with liver sausage emulsion and the ends of the sausage were clipped.

After cooking, the cooled sausage had a plump appearance and an attractive shape. Even after 4 weeks' storage under cold-room conditions (8°C, 76% relative humidity) no changes in the color or the flavor of the sausage could be detected.

What is claimed is:

1. A heat-shrinkable, laminated or coated plastic film which has, on one or both sides, a heat-sealable polyethylene, polypropylene or ethylene-propylene copolymer layer, and also has a layer of polyethylene terephthalate, polyamide or polypropylene, wherein the film has at least one layer of an inorganic-organic hybrid polymer or has an SiO_x layer.

2. A film as claimed in claim 1, wherein the thickness of the hybrid polymer layer is from 0.5 to 10 μm, preferably from 2 to 7 μm, particularly preferably about 5 μm.

3. A film as claimed in claim 1 or 2, wherein the thickness of the SiO_x layer is from 10 to 80 nm, preferably from 20 to 50 nm.

4. A film as claimed in one or more of claims 1 to 3, wherein the SiO_x layer is in direct contact with the nonsealable layer.

5. A film as claimed in one or more of claims 1 to 4, wherein the inorganic-organic hybrid polymer has the empirical formula $C_nH_mO_xSi_yMe_z$, where Me is a metal of the 3rd transition group, of the 4th main group or transition group, or of the 5th or 6th transition group of the Periodic Table, n is a number from 4 to 48, m is a number from 5 to 52, x is a number from 5 to 48 and y is a number from 2 to 16, and z is 1, with the proviso that the ratio m: (y+z) is less than 7, preferably less than 5.

6. A film as claimed in one or more of claims 1 to 5, wherein the inward-facing and the outward-facing layers were biaxially oriented prior to lamination with an area stretching ratio of from 1:2 to 1:20, preferably from 1:5 to 1:10.

7. A film as claimed in one or more of claims 1 to 6, wherein the nonsealable layer is composed of nylon-6, nylon-6,6, nylon-11, nylon-12, polyethylene terephthalate or polypropylene.

8. A film as claimed in one or more of claims 1 to 7, which has a shrinkage of from 5 to 15%, preferably about 10%, in both longitudinal and transverse directions (after storage for 15 min in water at 80°C).

9. A film tube with a welded seam, wherein the film tube has been produced from a film as claimed in one or more of claims 1 to 8.

10. A method for the use of the film tube as claimed in claim 9 as a casing for foods, preferably as a synthetic sausage-casing or as a casing for animal feed.

Abstract:

Shrinkable, laminated or coated film with improved barrier effectiveness, and a film tube produced therefrom with a welded seam

The invention relates to a heat-shrinkable, laminated or coated plastic film which has, on one or both sides, a heat-sealable polyethylene, polypropylene or ethylene-propylene copolymer layer, and also has a layer of polyethylene terephthalate, polyamide or polypropylene, which film has at least one layer of an inorganic-organic hybrid polymer or has an SiO_x layer. The film has high barrier effectiveness for (atmospheric) oxygen and water vapor. It is generally transparent, but may also have pigmentation and/or a print. Film tubes with a welded seam are produced from the flat film by heat-sealing. These are suitable as casings for foods, in particular for scalded-emulsion or cooked-meat sausages, and also as a casing for animal feed.